Quarterly Report No. 3

Copy No. 09

# A Study of the Decomposition Mechanism of Ammonium Perchlorate

Prepared by: ~~Departments of Chemistry and~~ Chemical ~~Engineering~~

Auburn Univ~~ersity~~

~~For the Period:~~ 1 Oct ~~19~~64 — 1 Jan ~~19~~65

Contract ~~No.~~ DA-01-009-ORD-1023(Z), ~~Part I~~

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Quarterly Progress Report No. 3

Birmingham Ordnance Contract DA-01-009-ORD-1023(Z), Part I, entitled "A Study of the Decomposition Mechanism of Ammonium Perchlorate".

For the period: 1 Oct. 1964 - 1 Jan. 1965.

1. During the period of this report ~~our~~ efforts continued with the making of differential thermal analysis (DTA) runs at various heating rates on ammonium perchlorate (AP) samples, where the samples were of various particle size, shape and either pure or contained selected additives.

A total of ~~one hundred and eight~~ DTA plots were made either on new specimens or for rechecking values recorded in Quarterly Report No. 2. Certain of these DTA runs were made with the sample under pressure of nitrogen gas to minimize the sublimation tendency of the AP.

2. The experimental techniques and equipment used were the same as described in ~~our~~ previous report, except that ~~we began mixing~~ very fine glass beads with the AP material. By using a smaller AP sample, the heat changes of the sample reaction do not influence the results as markedly and hence allow the temperature measuring devices to more accurately indicate the true temperature being experienced by the sample.

Glass beads were selected for the diluting of the material since they are non-conductors for electrons and should show no catalytic influence on the AP decomposition. In all cases we mixed the AP and glass beads in a 1:3 weight ratio.

The glass beads were Sign Beads, type 831A, Size B, wide angle and manufactured by Flex-O-Lite Manufacturing Company of St. Louis, Missouri.

Before being used the glass beads were washed with 3 normal hydrochloric acid solution, rinsed with distilled water and oven dried at 105 degrees C.

A DTA run on the glass beads alone vs. the alumdum reference indicated that they underwent no changes over the 25 to 450 degrees C. temperature range that could product exo- or endo-thermic peaks on the DTA plot.

3. Some of the results reported in Quarterly Report No. 2 were based upon too few determinations. In order to increase the reliability of the calculations, the following runs were made, consequently, the following data should be added to:

(A). Table IX of Quarterly Report No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-29-1 | 0.1975 | 248.9 | 2.11 | -11.769 |
| 2-29-2 | .2011 | 255.1 | 4.16 | -11.113 |
| 2-30-2 | .2034 | 256.8 | 10.30 | -10.213 |
| 2-31-3 | .2006 | 254.0 | 10.13 | -10.219 |
| 2-32-1 | .1989 | 258.7 | 9.87 | -10.263 |
| 2-33-1 | .1968 | 246.2 | 2.11 | -11.760 |

(B). Table X of Quarterly Report No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-31-2 | 0.2006 | 311.0 | 9.63 | -10.475 |
| 2-32-1 | .1989 | 318.7 | 9.36 | -10.530 |

(C). Table XI of Quarterly Report No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-29-1 | 0.1975 | 439.3 | 2.13 | -12.380 |
| 2-29-2 | .2011 | 459.9 | 3.83 | -11.851 |
| 2-30-2 | .2034 | 462.2 | 8.64 | -11.044 |
| 2-31-3 | .2006 | 453.5 | 10.00 | -10.874 |
| 2-32-1 | .1989 | 458.0 | 8.15 | -11.091 |
| 2-33-1 | .1968 | 443.0 | 2.25 | -12.336 |

(D). Table XII of Quarterly Report No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-30-1 | 0.2017 | 242.4 | 2.13 | -11.737 |
| 2-31-1 | .2005 | 248.9 | 4.47 | -11.021 |
| 2-31-2 | .2014 | 267.7 | 9.87 | -10.300 |

(E). Table XIII of Quarterly Report No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-31-2 | 0.2014 | 327.1 | 8.99 | -10.601 |

4. Erratum.

In Table XIII of Quarterly Report No. 2 the peak temperature for sample 2-25-2 should read 304.5 vice 343.0. The remaining terms in this horizontal line should be changed to °K = 577.7; $T_m^2 \times 10^{-5} = 3.34$; $\text{Rate}/T_m^2 \times 10^5 = 1.260$; $1/T_m \times 10^3 = 1.732$; $\ln(\text{Rate}/T_m^2) = -11.270$.

5. In Table XVIII of Quarterly Report No. 2 for sample - Fine AP, peak No. 2, the slope has been computed to be $-15.84 \times 10^3$ and the activation energy therefore is 30.46 kcal./mole.

6. In order to minimize the tendency of the AP sample to sublime from the hot to the cooler portion of the sample tube, DTA determinations were conducted under a nitrogen atmosphere where the pressure was maintained at 60 mm. of Hg in excess of atmospheric pressure.

The DTA plots showed three peaks. Peak 1 is the endotherm associated with the change in crystal structure. Peak 2 and 4 (we use 4 instead of 3 for designating this peak so as to indicate that is is the same peak so numbered on the DTA plots run against air pressure and shown in Fig. 4 of Quarterly Report No. 2) are the low and high temperature exotherms.

In the following tables are recorded the results of these runs and the last table summarizes the slope of the curves plotted from these data as well as the calculated activation energies.

Table 6-1

Material - Fine AP; Peak No. 1

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-40-2 | 0.2010 | 247.8 | 4.47 | -11.014 |
| 2-41-1 | .2014 | 246.6 | 2.34 | -11.657 |
| 2-41-2 | .2034 | 267.7 | 10.10 | -10.274 |
| 2-61-1 | .1989 | 244.2 | 2.10 | -11.756 |
| 2-62-1 | .2006 | 257.2 | 9.20 | -10.328 |
| 2-62-2 | .2003 | 250.5 | 4.20 | -11.087 |

Table 6-2

Material - Fine AP; Peak No. 2

| Sample No. | Sample Wt., | Peak T(°C) | Rate | ln(Rate/$T_m^2$) |
|---|---|---|---|---|
| 2-40-2 | 0.2010 | 298.7 | 4.43 | -11.200 |
| 2-41-2 | 0.2034 | 330.9 | 8.80 | -10.620 |
| 2-61-2 | 0.1989 | 310.1 | 2.00 | -12.044 |
| 2-62-2 | 0.2006 | 318.6 | 9.80 | -12.000 |

Table 6-3

Material - Fine AP; Peak No. 4

| Sample No. | Sample Wt. | Peak T(°C) | Rate | ln(Rate/$T_m^2$) |
|---|---|---|---|---|
| 2-40-2 | 0.2010 | 443.0 | 4.37 | -11.673 |
| 2-41-1 | 0.2019 | 430.2 | 3.13 | -12.350 |
| 2-41-2 | 0.2034 | 479.0 | 8.40 | -11.117 |
| 2-61-1 | 0.1989 | 420.6 | 2.10 | -12.343 |
| 2-62-1 | 0.2006 | 459.8 | 11.00 | -10.796 |
| 2-62-2 | 0.2003 | 443.8 | 4.20 | -11.715 |

Table 6-4

Material - Medium AP; Peak No. 1

| Sample No. | Sample Wt. | Peak T(°C) | Rate | ln(Rate/$T_m^2$) |
|---|---|---|---|---|
| 2-42-1 | 0.2002 | 241.4 | 2.23 | -11.685 |
| 2-42-2 | 0.2004 | 245.8 | 4.21 | -11.067 |
| 2-42-3 | 0.2015 | 258.7 | 11.70 | -10.094 |
| 2-60-3 | 0.2024 | 253.3 | 4.00 | -11.146 |
| 2-61-2 | 0.2047 | 252.10 | 2.20 | -11.740 |
| 2-63-1 | 0.2005 | 250.5 | 10.00 | -10.200 |

Table 6-5

Material - Medium AP, Peak No. 3

| Sample No. | Sample Wt. | Peak ($^{o}$C) | Rate | ln(Rate/$T_m^2$) |
|---|---|---|---|---|
| 2-42-2 | 0.2004 | 293.0 | 4.11 | -11.264 |
| 2-42-3 | 0.2015 | 318.0 | 8.72 | -10.599 |
| 2-60-3 | 0.2024 | 310.1 | 4.10 | -11.526 |
| 2-61-2 | 0.2047 | 315.2 | 2.00 | -12.061 |
| 2-63-1 | 0.2005 | 313.0 | 9.40 | -10.506 |

Table 6-6

Material - Medium AP; Peak No. 4

| Sample No. | Sample Wt. | Peak T($^{o}$C) | Rate | ln(Rate/$T_m^2$) |
|---|---|---|---|---|
| 2-42-1 | 0.2002 | 434.4 | 2.18 | -12.983 |
| 2-42-2 | 0.2004 | 441.1 | 3.95 | -11.769 |
| 2-42-3 | 0.2015 | 456.8 | 10.48 | -10.336 |
| 2-60-3 | 0.2024 | 458.6 | 4.10 | -11.770 |
| 2-61-2 | 0.2047 | 439.3 | 2.30 | -12.350 |
| 2-63-1 | 0.2005 | 446.8 | 8.70 | -10.395 |

Table 6-7

Material - Coarse AP; Peak No. 1

| Sample No. | Sample Wt. | Peak ($^{o}$C) | Rate | ln(Rate/$T_m^2$) |
|---|---|---|---|---|
| 2-44-1 | 0.2023 | 248.9 | 2.20 | -11.727 |
| 2-45-1 | 0.2003 | 263.4 | 3.95 | -11.200 |
| 2-45-2 | 0.2007 | 254.3 | 10.50 | -10.135 |
| 2-59-3 | 0.2006 | 250.1 | 4.30 | -11.050 |
| 2-60-1 | 0.2031 | 248.2 | 2.20 | -11.725 |
| 2-60-2 | 0.2013 | 254.4 | 10.50 | -10.135 |

**Table 6-8**

**Material - Coarse AP; Peak No.2**

| Sample No. | Sample Wt. | Peak T(°C) | Rate | ln(Rate/$T_m^2$) |
|---|---|---|---|---|
| 2-45-2 | 0.2007 | 517.2 | 9.00 | -10.564 |
| 2-45-1 | 0.2003 | 529.8 | 4.04 | -11.408 |
| 2-59-3 | 0.2006 | 296.8 | 4.10 | -11.270 |
| 2-60-1 | 0.2031 | 303.8 | 2.10 | -11.950 |
| 2-60-2 | 0.2013 | 514.8 | 8.90 | -10.300 |

Table 6-9

Material - Coarse AP; Peak No. 4

| Sample No. | Sample Wt. | Peak T(°C) | Rate | ln(Rate/$T_m^2$) |
|---|---|---|---|---|
| 2-44-1 | 0.2023 | 439.3 | 2.12 | -12.585 |
| 2-45-2 | 0.2007 | 451.2 | 9.13 | -10.960 |
| 2-45-1 | 0.2003 | 472.7 | 4.07 | -11.84[illegible] |
| 2-59-3 | 0.2006 | 458.0 | 4.10 | -11.778 |
| 2-60-1 | 0.2031 | 435.5 | 1.90 | -12.496 |
| 2-60-2 | 0.2013 | 147.5 | 9.20 | -10.941 |

**Table 6-10**

Summary of fine, medium and coarse AP DTA vs. nitrogen pressure and the computed activation energies.

| Sample | Peak No. | Slope $\times 10^{-3}$ | Act. Energy (Kcal./mole) |
|---|---|---|---|
| Fine AP | 1 | -29.7 | 56.96 |
| Fine AP | 2 | -13.8 | 26.49 |
| Fine AP | 4 | - 9.9 | 19.07 |
| Medium AP | 1 | -29.5 | 56.55 |
| Medium AP | 2 | - 6.5 | 12[illegible] |
| Medium AP | 4 | -19.0 | [illegible] |
| Coarse AP | 1 | -38.0 | 72.[illegible] |
| Coarse AP | 2 | -15.3 | 29.[illegible] |
| Coarse AP | 4 | -35.3 | 67.[illegible] |

7. The minimum size of sample holder that we have been able to construct and employ (pictured as Fig. 3 of Quarterly Report No. 2) required approximately 200 mg of sample of AP to adequately cover the thermocouple so that it would give sensible voltage values of EMF within the limits of amplification of our equipment.

It was felt that the heat liberated by such a large sample in the very short time of reaction was of such magnitude that it tended to make the sample subject to a temperature value not represented by or recorded as block temperature.

To overcome this difficulty it was decided to use a smaller AP sample but to provide the necessary volume of sample to cover the thermocouple adequately by adding an inert diluting material to the AP, namely very fine glass beads.

Unless otherwise noted the sample was made up by mixing 300 mg of glass beads with 100 mg of AP.

In order that the effect of the glass beads on the calculated results of activation energy might be noted, we made determinations on the medium size AP previously reported on in Quarterly Report No. 2 and on the No 4 Huntsville Sample, both versus air and a nitrogen atmosphere at 60 mm of Hg in excess of air pressure, and these results are reported in the following tables. (Note - the measurements on the Huntsville No. 4 without glass beads are recorded in paragraph 6 of this report.)

Table 7-1

Material Medium AP. Peak No 1 vs. Air

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-71-1 | 3/1 | 241.4 | 2.24 | -11.6801 |
| 2-71-2 | 3/1 | 245.4 | 4.47 | -11.0041 |
| 2-72-2 | 3/1 | 250.9 | 10.51 | -10.1711 |

Table 7-2

Material - Medium AP; Peak No. 2; vs. Air

| Sample No. | Sample Wt. | Peak (°C) | Rate | $\ln(\text{Rate}/t_m^2)$ |
|---|---|---|---|---|
| 2-72-2 | 3/1 | 350.0 | 2.02 | -10.8076 |
| 2-73-1 | 0.1995 | 321.6 | 3.66 | -11.7033 |

**Table 7-3**

Material - Medium AP; Peak No. 4; vs. Air

| Sample No. | Sample Wt. | Peak (°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-71-1 | 3/1 | 409.4 | 2.00 | -12.3585 |
| 2-71-2 | 3/1 | 440.0 | 4.25 | -11.6924 |
| 2-72-2 | 3/1 | 462.3 | 10.00 | -10.9024 |
| 2-73-1 | 0.1995 | 465.8 | 2.00 | -12.4900 |

**Table 7-4**

Material - $H_4$; Peak No. 1; vs. Air

| Sample No. | Sample Wt. | Peak (°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-64-1 | 3/1 | 256.8 | 2.34 | -11.6954 |
| 2-64-2 | 3/1 | 258.8 | 4.28 | -11.0992 |
| 2-67-1 | 3/1 | 251.7 | 10.40 | -10.1844 |

**Table 7-5**

Material - $H_4$; Peak No. 2; vs. Air

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-64-1 | 3/1 | 289.1 | 2.08 | -11.9514 |
| 2-64-2 | 3/1 | 330.0 | 4.18 | -11.3742 |
| 2-67-1 | 3/1 | 323.3 | 8.67 | -10.5994 |

**Table 7-6**

Material - $H_4$; Peak No. 4; vs. Air

| Sample No. | Sample Wt. | Peak (°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-64-1 | 3/1 | 433.6 | 2.13 | -12.4851 |
| 2-64-2 | 3/1 | 467.5 | 4.32 | -11.7518 |
| 2-67-1 | 3/1 | 470.9 | 8.47 | -11.0875 |

**Table 7-7**

Material - $H_4$; Peak No. 1; vs. Nitrogen

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|---|
| 2-65-1 | 3/1 | 240.2 | 2.21 | -11.8089 |
| 2-66-1 | 3/1 | 241.0 | 4.29 | -11.0283 |
| 2-67-2 | 3/1 | 255.6 | 11.94 | -10.0613 |

**Table 7-8**

Material - $H_4$; Peak No. 2; vs. Nitrogen

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|---|
| 2-65-1 | 3/1 | 282.5 | 1.94 | -11.9777 |
| 2-66-1 | 3/1 | 303.3 | 3.97 | -11.3350 |
| 2-67-2 | 3/1 | 324.9 | 8.73 | -10.3803 |

**Table 7-9**

Material - $H_4$; Peak No. 4; vs. Nitrogen

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|---|
| 2-66-1 | 3/1 | 422.9 | 4.00 | -11.7046 |
| 2-67-2 | 3/1 | 475.3 | 11.00 | -10.3594 |

Table 7-10

Summary of activation energies calculated for two samples to note effect of using glass beads.

| Sample | Atmosphere | Peak No. | Slope x $10^{-3}$ | Act. Energy (kcal./mole) |
|---|---|---|---|---|
| Medium AP | Air | 1 | -45.8 | 85.0 |
| Medium AP | Air | 2 | -16.46 | 30.7 |
| Medium AP | Air | 4 | -15.00 | 28.0 |
| H4 | Air | 1 | -94.0 | 186.8 |
| H4 | Air | 2 | - 9.0 | 17.9 |
| H4 | Air | 4 | -21.6 | 42.9 |
| H4 | N2 | 1 | -25.8 | 51.3 |
| H4 | N2 | 2 | -11.0 | 21.9 |
| H4 | N2 | 4 | - 9.5 | 18.9 |

8. In order to determine the influence of such things as particle size, shape of particle and added conditioners upon the activation energies associated with the decomposition of AP, we were furnished the following samples by Mr. Huskins of the AMC Propulsion Laboratory, Redstone Arsenal, Huntsville, Alabama.

These samples will be designated H-1 through H-6 and their specifications are as follows:

H-1: 400 micron, rounded AP, 99.2% minimum AP, conditioned with tricalcium phosphate (TCP), lot no. 4080.

H-2: 45 micron, rounded AP, 99.2% minimum AP, conditioned with TCP, lot no. 1030-194-1.

H-3: 17 micron, ground AP, conditioned with TCP, lot no. 2153.

H-4: 180 micron, unground AP, conditioned with TCP, lot no. 2153.

H-5: 8 micron, ground AP, conditioned with TCP.

H-6: 90 micron, rounded AP, conditioned with TCP, 99.2% minimum AP, lot no. 1075-33-11.

In the following tables are the peak temperatures measured for these samples at different heating rates. All of these samples were run versus air pressure, and without glass beads as a dilutant. A table summarizing the calculated activation energies of these samples concludes this paragraph.

Table 8-1

Material - AP H-1; Peak No. 1

| Sample No. | Sample Wt. | Peak (°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-45-3 | 0.2004 | 248.6 | 4.48 | -11.015 |
| 2-46-1 | 0.1997 | 254.9 | 10.39 | -10.1973 |
| 2-54-1 | 0.2033 | 251.3 | 2.2 | -11.720 |
| 2-72-1 | 0.1943 | 243.4 | 2.37 | -11.620 |

Table 8-2

Material - AP, H-1; Peak No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-45-3 | 0.2004 | 290.7 | 1.11 | -11.2566 |
| 2-46-1 | 0.1997 | 305.0 | 3.12 | -10.5092 |
| 2-54-1 | 0.2033 | 284.9 | 2.1 | -11.3073 |
| 2-72-1 | 0.1943 | 278.2 | 1.55 | -11.3495 |

Table 8-3

Material - AP, H-1; Peak No. 4

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-54-1 | 0.2033 | 434.8 | 8.10 | 12.385 |
| 2-45-3 | 0.2004 | 445.0 | 4.59 | -11.644 |
| 2-46-1 | 0.1997 | 440.8 | 10.36 | -10.828 |

Table 8-4

Material - AP, H-2; Peak N 1

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-46-2 | 0.2013 | 241.9 | 4.47 | -10.0912 |
| 2-48-2 | 0.2002 | 259.0 | 8.99 | -10.2623 |
| 2-56-3 | 0.2029 | 245.0 | 3.29 | -11.7120 |

Table 8-5

Material - AP, H-2; Peak No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-46-2 | 0.2013 | 287.3 | 1.13 | -11.5811 |
| 2-48-2 | 0.2002 | 316.9 | 3.63 | -10.8754 |
| 2-56-3 | 0.2029 | 279.3 | 0.77 | -11.7277 |

Table 8-6

Material - AP, H-2; Peak No. 4

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-46-2 | 0.2013 | 427.4 | 3.87 | -11.7505 |
| 2-48-2 | 0.2002 | 449.8 | 8.77 | -10.9958 |
| 2-56-3 | 0.2029 | 429.4 | 2.10 | -12.3673 |

Table 8-7

Material - AP, H-3; Peak No. 1

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-50-1 | 0.2002 | 248.6 | 4.3 | -11.0560 |
| 2-50-2 | 0.2028 | 247.7 | 2.2 | -11.7224 |
| 2-50-3 | 0.2002 | 255.7 | 10.4 | -10.1996 |

Table 8-8

Material - AP, H-3; Peak No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-50-1 | 0.2002 | 299.5 | 4.3 | -11.2600 |
| 2-50-2 | 0.2028 | 291.9 | 2.1 | -11.9316 |
| 2-50-3 | 0.2002 | 325.7 | 9.3 | -11.5708 |

Table C-9

Material - AP, H-3; Peak No. 4

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-50-1 | 0.2002 | 428.8 | 4.3 | -11.5490 |
| 2-50-2 | 0.2028 | 424.4 | 2.0 | -12.4019 |
| 2-50-3 | 0.2002 | 446.0 | 10.89 | -10.7689 |

Table 8-10

Material - AP, H-4; Peak No. 1

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-49-2 | 0.2055 | 247.8 | 4.5 | -11.0072 |
| 2-53-1 | 0.2010 | 244.2 | 2.5 | -11.5812 |
| 2-56-1 | 0.2003 | 264.6 | 9.9 | -10.3883 |

Table 8-11

Material - AP, H-4; Peak No.2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-49-2 | 0.2055 | 294.9 | 4.1 | -11.2730 |
| 2-53-1 | 0.2010 | 288.8 | 2.1 | -11.8485 |
| 2-56-1 | 0.2003 | 319.5 | 9.1 | -10.5611 |

Table 8-12

Material - AP , H-4; Peak No. 4

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-49-2 | 0.2055 | 446.8 | 4.38 | -11.6873 |
| 2-53-1 | 0.2010 | 439.5 | 2.10 | -12.3954 |
| 2-56-1 | 0.2003 | 471.5 | 11.0 | -10.3879 |

Table 8-13

Material - AP, H-5; Peak No. 1

| Sample No. | Sample Wt. | Peak (°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|---|
| 2-54-2 | 0.2003 | 251.3 | 4.5 | -11.0668 |
| 2-58-1 | 0.2000 | 242.2 | 2.0 | -11.7968 |
| 2-58-2 | 0.2008 | 260.7 | 9.7 | -10.2801 |

Table 8-14

Material - AP, H-6; Peak No. 4

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|---|
| 2-54-2 | 0.2003 | 487.5 | 4.1 | -11.6752 |
| 2-58-1 | 0.2000 | 492.6 | 1.9 | -12.7899 |
| 2-58-2 | 0.2008 | 488.1 | 10.2 | -10.8540 |

Table 8-15

Material - AP, H-6; Peak No. 1

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|---|
| 2-56-2 | 0.2000 | 253.0 | 4.4 | -11.0497 |
| 2-58-3 | 0.2012 | 245.0 | 2.6 | -11.7121 |
| 2-59-1 | 0.2004 | 257.6 | 10.7 | -10.1786 |

Table 8-16

Material - AP, H-6; Peak No. 2

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|---|
| 2-56-2 | 0.2000 | 339.6 | 4.2 | -11.0447 |
| 2-58-3 | 0.2012 | 330.3 | 2.1 | -11.7889 |
| 2-59-1 | 0.2004 | 346.3 | 8.9 | -10.0875 |

Table 8-17

Material - AP, H-6; Peak No. 4

| Sample No. | Sample Wt. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|---|
| 2-56-2 | 0.2000 | 483.5 | 4.3 | -11.7500 |
| 2-58-3 | 0.2012 | 434.4 | 2.4 | -12.3700 |
| 2-59-1 | 0.2004 | 485.4 | 8.6 | -11.0347 |

Table 8-18

Summary of activation energies calculated for samples supplied by Propulsion Laboratory.

| Sample | Peak No. | Slope x $10^{-3}$ | Act. Energy (kcal./mole) |
|---|---|---|---|
| H1 | 1 | -29.7 | 59.0 |
| H1 | 2 | -16.6 | 33.0 |
| H1 | 4 | -68.0 | 135.5 |
| H2 | 1 | -30.2 | 60.1 |
| H2 | 3 | - 9.3 | 18.5 |
| H2 | 4 | -28.0 | 55.5 |
| H3 | 1 | -56.0 | 111.2 |
| H3 | 2 | -11.0 | 21.8 |
| H3 | 4 | -37.5 | 74.5 |
| H4 | 1 | -17.6 | 35.0 |
| H4 | 2 | - 7.2 | 14.3 |
| H4 | 4 | -23.6 | 46.9 |
| H5 | 1 | -22.8 | 45.3 |
| H5 | 4 | -15.4 | 30.6 |
| H6 | 1 | -35.0 | 69.5 |
| H6 | 2 | - 9.1 | 18.1 |
| H6 | 4 | -30.0 | 59.5 |

9. For the purpose of determining the influence of catalytic agents on the activation energies of the AP decomposition, DTA runs were made wherein a given amount of an added compound was mixed with the AP.

Two materials, finely powdered aluminum oxide and iron (III) oxide, have been studied for their catalytic effect on the AP decomposition reactions.

In all cases 0.10 g of AP was mixed with the glass beads in a 3:1 weight ratio and then 5% by weight of the AP equalled the weight of the added catalytic agent. All of these were physically stirred together for a length of time [illegible] distribution of catalyst through out the mixture.

The following tables give the measured values for the DTA runs and the final table summarizes the computed activation energies of the reactions.

Table 9-1

Material - Fine AP, with $Fe_2O_3$; Peak No. 1; vs Air at atmospheric pressure

| Sample No. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|
| 2-85-1 | 247.0 | 2.1 | -11.7664 |
| 2-85-2 | 248.9 | 14.9 | - 9.8210 |
| 2-84-2 | 251.3 | 4.2 | -11.0375 |

Table 9-2

Material - Fine AP, with $Fe_2O_3$; Peak No. 4; vs. air at atmospheric pressure.

| Sample No. | Peak (°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|
| 2-85-1 | 352.9 | 2.0 | -12.1759 |
| 2-85-2 | 396.2 | 7.9 | -10.9459 |
| 2-84-2 | 389.1 | 4.0 | -11.5487 |

Table 9-3

Material - Fine AP, with $Fe_2O_3$; Peak No. 1; vs. $N_2$ at 60 mm. excess pressure.

| Sample No. | Peak T(°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|
| 2-86-1 | 250.0 | 12.2 | -10.[illegible] |
| 2-91-1 | 246.2 | 8.9 | -11.[illegible] |
| 2-91-2 | 248.9 | 4.1 | -12.[illegible] |

Table 9-4

Material - Fine AP, with $Fe_2O_3$; Peak No. 4; vs. $N_2$ at 60 mm. excess pressure

| Sample No. | Peak (°C) | Rate | $\ln(\text{Rate}/T_m^2)$ |
|---|---|---|---|
| 2-86-1 | 397.4 | 8.0 | -10.[illegible] |
| 2-91-1 | 357.8 | 2.0 | -12.[illegible] |
| 2-91-2 | 380.0 | 3.8 | -11.[illegible] |

**Table 9-5**

Material - Medium AP, with $Fe_2O_3$; Peak No. 1; vs. Air

| Sample No. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-79-1 | 250.1 | 13.7 | - 9.9042 |
| 2-82-3 | 252.9 | 4.3 | -11.063 |
| 2-82-2 | 250.9 | 2.2 | -11.7167 |
| 2-81-1 | 250.1 | 2.2 | -11.7137 |

**Table 9-6**

Material - Medium AP, with $Fe_2O_3$; Peak No. 4; vs. Air

| Sample No. | Peak (°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-79-1 | 401.9 | 9.13 | -10.9181 |
| 2-82-3 | 400.0 | 4.13 | -11.6057 |
| 2-82-2 | 372.9 | 2.13 | -12.1857 |
| 2-81-1 | 372.5 | 2.13 | -12.1843 |

**Table 9-7**

Material - Medium AP, with $Fe_2O_3$; Peak No. 1; vs. $N_2$ at 60 mm. excess pressure.

| Sample No. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-81-1 | 252.5 | 13.50 | - 9.9236 |
| 2-83-2 | 251.7 | 4.31 | -11.0655 |
| 2-83-1 | 251.3 | 2.11 | -11.7780 |

Table 9-8

Material - Medium AP, with $Fe_2O_3$; Peak No. 4; vs. $N_2$ at 60 mm. excess pressure.

| Sample No. | Peak (°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-81-1 | 419.1 | 8.58 | -10.9540 |
| 2-83-2 | 395.1 | 4.13 | -11.5911 |
| 2-83-1 | 373.6 | 2.13 | -12.1876 |

Table 9-9

Material - Fine AP, with $Al_2O_3$; Peak No. 1; vs. Air

| Sample No. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-79-2 | 249.7 | 4.34 | -11.0509 |
| 2-80-2 | 252.1 | 13.80 | - 9.9082 |
| 2-81-2 | 252.5 | 2.47 | -11.6250 |

Table 9-10

Material - Fine AP, with $Al_2O_3$; Peak No. 4; vs. Air

| Sample No. | Peak (°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-79-2 | 396.3 | 4.00 | -11.3286 |
| 2-80-2 | 418.0 | 8.00 | -10.9973 |
| 2-81-2 | 377.3 | 2.25 | -12.1160 |

Table 9-11

Material - Fine AP, with $Al_2O_3$; Peak No. 1; vs. $N_2$ at 60 mm. excess pressure.

| Sample No. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-78-2 | 255.6 | 4.16 | -11.1154 |
| 2-78-3 | 251.3 | 11.45 | -10.0868 |
| 2-80-1 | 253.6 | 2.37 | -11.6703 |

Table 9-12

Material - Fine AP, with $Al_2O_3$; Peak No. 4; vs. $N_2$ at 60 mm. excess pressure.

| Sample No. | Peak (°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-78-2 | 388.7 | 4.13 | -11.5718 |
| 2-78-3 | 419.1 | 9.75 | -10.8028 |
| 2-80-1 | 375.9 | 2.00 | -12.2547 |

Table 9-13

Material - Medium AP, with $Al_2O_3$; Peak No. 1; vs. Air

| Sample No. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-76-1 | 247.8 | 4.34 | -11.0434 |
| 2-76-2 | 251.7 | 12.70 | - 9.9843 |
| 2-77-2 | 248.5 | 1.97 | -11.6356 |

Table 9-14

Material - Medium AP, with $Al_2)_3$; Peak No. 4; vs. Air

| Sample No. | Peak (°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-76-1 | 404.9 | 3.88 | -11.5826 |
| 2-76-2 | 433.6 | 10.38 | -10.7814 |
| 2-77-2 | 386.1 | 2.25 | -12.1713 |

Table 9-15

Material - Medium AP, with $Al_2O_3$; Peak No. 1; vs. $N_2$ at 60 mm. excess pressure.

| Sample No. | Peak T(°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-76-3 | 252.1 | 4.34 | -11.0598 |
| 2-77-1 | 252.5 | 13.03 | - 9.9621 |
| 2-78-1 | 252.1 | 2.08 | -11.7954 |

Table 9-16

Material - Medium AP, with $Al_2O_3$; Peak No. 4; vs. $N_2$ at 60 mm. excess pressure.

| Sample No. | Peak (°C) | Rate | $\ln(Rate/T_m^2)$ |
|---|---|---|---|
| 2-76-3 | 397.0 | 4.00 | -11.6283 |
| 2-77-1 | 435.9 | 8.00 | -11.0484 |
| 2-78-1 | 371.4 | 2.13 | -12.1310 |

Table 9-17

Summary of activation energies calculated for AP with added catalysts.

| Sample | Atmosphere | Peak | Slope $\times 10^{-3}$ | Act. Energy (kcal./mole) |
|---|---|---|---|---|
| Fine AP/$Fe_2O$ | Air | 1 | -90.0 | 178.8 |
| " | Air | 4 | -11.2 | 22.05 |
| " | $N_2$ | 1 | - 260 | 517.0 |
| " | $N_2$ | 4 | -15.1 | 30.0 |
| Medium AP/ $Fe_2O_3$ | Air | 1 | - 7.7 | 15.3 |
| " | Air | 4 | -13.8 | 27.5 |
| " | $N_2$ | 1 | - 421 | 836.0 |
| " | $N_2$ | 4 | -12.2 | 24.0 |
| Fine AP/$Al_2O_3$ | Air | 1 | -134.5 | 267.0 |
| " | Air | 4 | -12.9 | 25.7 |
| " | $N_2$ | 1 | - 92 | 182.8 |
| " | $N_2$ | 4 | -14.8 | 29.5 |
| Medium AP/ $Al_2O_3$ | Air | 1 | -12.5 | 24.8 |
| " | Air | 4 | -13.6 | 26.9 |
| " | $N_2$ | 1 | -83.9 | 166.7 |
| " | $N_2$ | 4 | - 9.0 | 17.9 |

10. It must be emphasized that the data quoted in these Quarterly Reports represent all runs made and is not to be considered the final answer in each case. Such data will be subject to further rechecking and consideration. In some cases it may be necessary, in light of new measurements, to alter, discard or modify some of these recorded values.

James E. Land,
Project Supervisor